Undergraduate Semester – VI

MJC – 12 (T): Physical Chemistry: Quantum Chemistry & Spectroscopy (T)

Quantum Chemistry & Spectroscopy
Theory: 4 credits

Unit 1: Elementary Quantum Mechanics

Introduction:

Classical mechanics is obeyed by microscopic particles such as planets and rigid bodies. It was formulated by Sir Issac Newton (1642-1727) in the seventeenth century. However, microscopic particles such as electrons, protons, atoms molecules show wave duality. They do not obey Newtonian dynamics. They obey quantum mechanics (wave mechanics), a key feature of which is quantization of energy and angular momentum.

From your earlier knowledge, you know that Bohr's theory of hydrogen atom enabled calculation of radii and energies associated with the permissible orbits in the hydrogen atom. The values calculated were found to be in good agreement with experimental values. However, the use of spectroscope of high resolving power reveals the presence of fine structures in the spectra of hydrogen. Bohr's theory could not explain the occurrence of these fine spectral lines.

Black Body Radiation and Quantum Theory:

Radiation is defined as a wave that consists of oscillating electric and magnetic field; hence, it is also called electromagnetic wave. It is characterised by its wavelength and frequency (number of oscillations per second) which are related as c, where c is the velocity of the wave. The value of c is generally 3×10^{8} ms^{-1}.

Radiation is emitted by any solid at any temperature due to the vibrations of its constituent particles. At low temperatures, the emitted radiation is of low frequency (long wavelength) and lies mainly in the infrared region. The human body also emits infrared radiation, but the amount of radiation is very small. As the temperature is increased, not only does the amount of radiation increase, but radiation of higher frequencies (shorter wavelengths) is also emitted. At any given temperature, the radiation emitted by a solid consists of a continuous range of frequencies, in contrast to gases, which produce line spectra.

Different solids emit radiation at different rate at the same temperature; the rate is maximum when the solid is perfectly black (black body). By definition, a black body can absorb all the radiations that falls on it. In practice, a hollow enclosure having a small hole is the nearest approach to a black body because the radiation entering the chamber through the hole is absorbed completely due to repeated reflections inside the enclosure. Radiations emerging from the small hole of such a hollow enclosure is, therefore, called 'black body radiation'. The intensity of radiation, i.e., that total radiation emitted per unit surface area, from a black body depends only on temperature (T) and is independent of the nature of the solid.

Distribution of Energy in the Black Body Radiation:

The radiation emitted by a black body is not confined to a single wavelength but is spread over a wide spectrum of wave lengths. the distribution of radiant energy over the different frequencies is described in term of a function which denotes the radiant density (amount of radiation per unit volume of the black body chamber) in the frequency range, say υ and $\upsilon + d\upsilon$. Experimentally, it is found that any temperature T the energy density increases with wavelength A^0, reaches a maximum and then falls off to zero. As temperature increases the point of maximum shifts to higher frequency (shorter wavelength) side. The experimental dependence of the energy density on temperature and wave length (λ) is shown in Fig. 1.

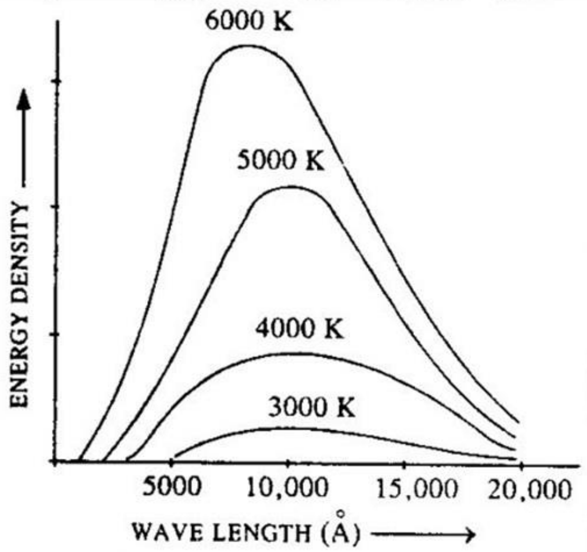

Fig. 1. Plots of energy density versus wave length for black body radiations at different temperatures.

Fig.1: Dependence of energy density on wavelength and temperature.